

Contract NASW-4698  
MCR-93-1339

**ANNUAL TECHNICAL REPORT**

**June 1993**

**MARS AQUEOUS CHEMISTRY  
EXPERIMENT**

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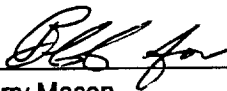
ANNUAL TECHNICAL REPORT  
YEAR 1

FOR THE

MARS AQUEOUS CHEMISTRY EXPERIMENT

JUNE 1993

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## **MACE ANNUAL TECHNICAL REPORT -- Year 1**

### **Progress: June 1992 to June 1993**

#### **INTRODUCTION**

This report details the progress for contract NASW-4698, the Mars Aqueous Chemistry Experiment (MACE), a part of the Planetary Instrument Definition and Development Program (PIDDP). The progress reported in this document is for the period beginning June 1992 through June 1993, and comprises the first year Annual Technical Report.

MACE is designed to conduct a variety of measurements on regolith samples, encompassing mineral phase analyses, chemical interactions with H<sub>2</sub>O, and physical properties determinations. From these data, much can be learned or inferred regarding the past weathering environment, the contemporaneous soil micro-environments, and the general chemical and physical state of the Martian regolith. By analyzing both soil and duricrust samples, the nature of the latter may become more apparent. Sites may be characterized for comparative purposes and criteria could be set for selection of high priority materials on future sample return missions.

Progress for the first year MACE PIDDP is reported in two major areas of effort:

- (1) fluids handling concepts, definition, and breadboard fabrication
- (2) aqueous chemistry ion sensing technology and test facility integration

#### **Fluids Handling Breadboard**

A fluids handling breadboard was designed, fabricated, and tested at Mars ambient pressure. The breadboard allows fluid manipulation scenarios to be tested under the reduced pressure conditions expected in the Martian atmosphere in order to validate valve operations, orchestrate analysis sequences, investigate sealing integrity, and to demonstrate efficacy of the fluid handling concept. Additional fluid manipulation concepts have also been developed based on updated MESUR spacecraft definition.

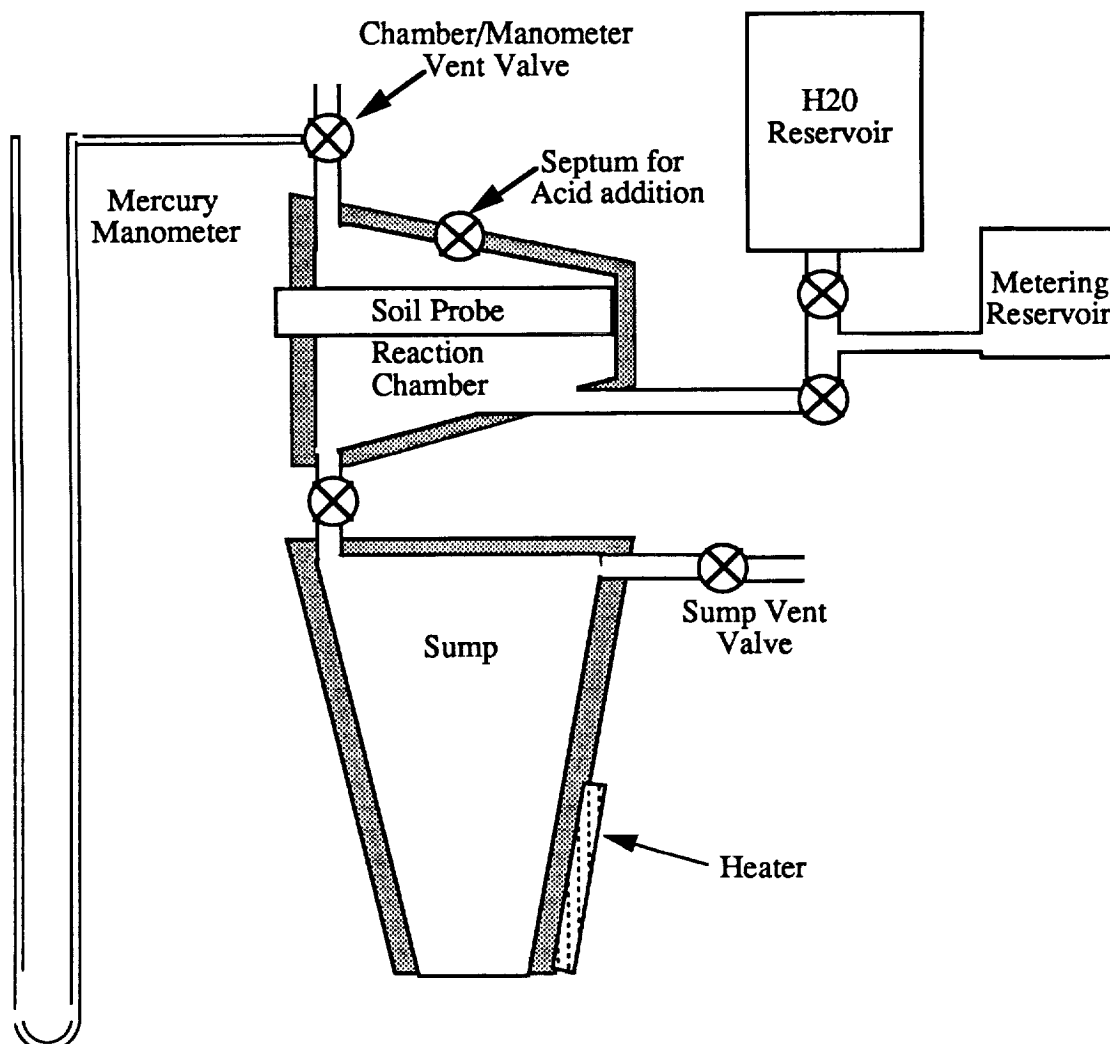
#### **Ion Selective Electrode Test Facility**

The Mars Aqueous Chemistry Experiment ISE facility was designed as a testbed to develop a multifunction interface for measurements of chemical ion concentrations in aqueous solution. The interface allows acquisition of real time data concerning the kinetics and heats of salt dissolution, and transient response to calibration and solubility events. An array of Ion Selective Electrodes (ISE) has been interfaced and preliminary calibration studies performed.

### **YEAR 1 PROGRESS**

#### **Fluids Handling**

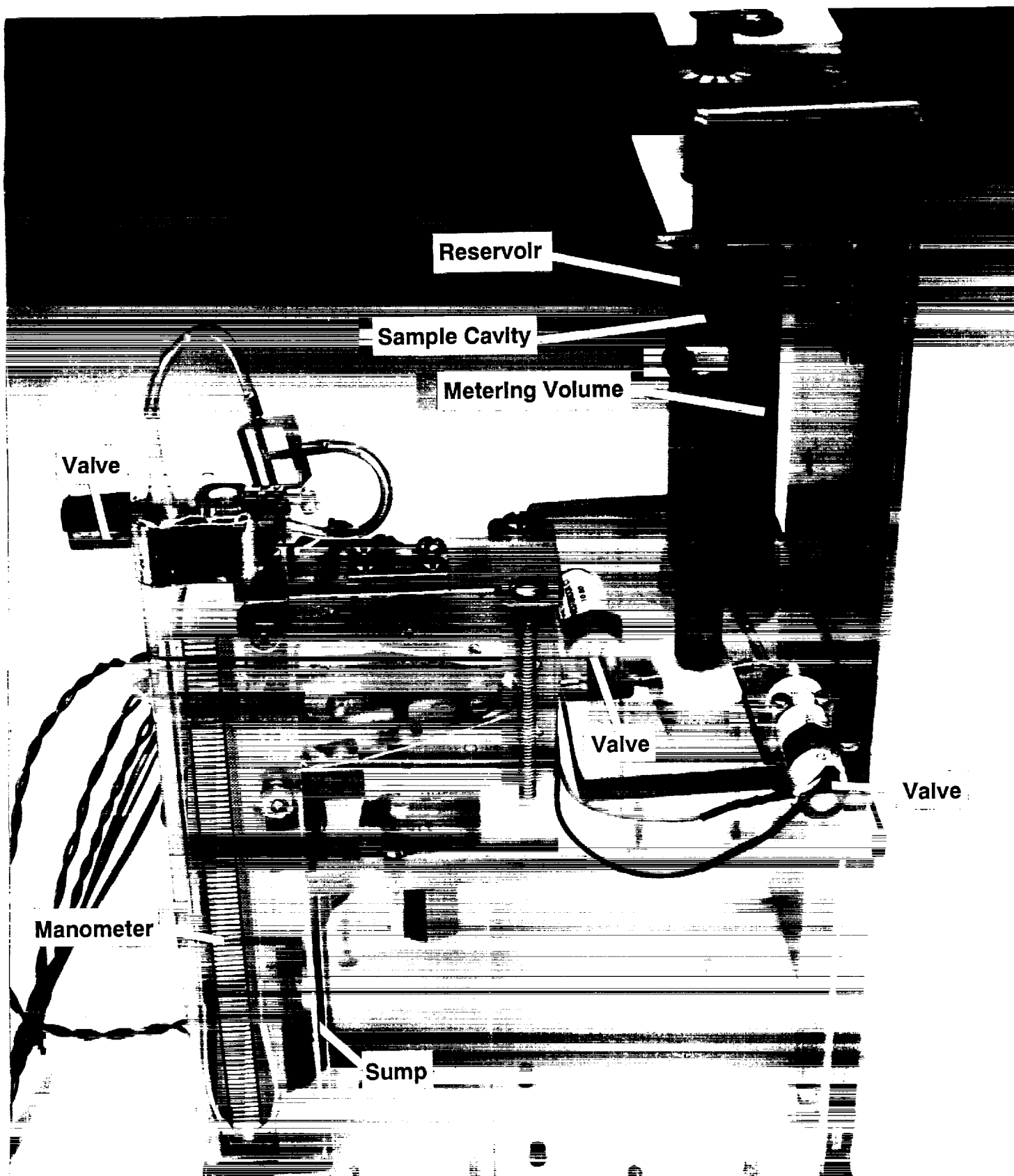
The MACE breadboard development has produced three units for demonstration of fluid handling. The first two units were constructed with manual valves and were primarily used for conceptual investigations at Earth nominal atmospheric pressure. The first unit was used as a visual aid to demonstrate the experiment concept and fluid handling. The second had electrodes installed for testing the resistivity of a simulated soil sample, an upgraded valve configuration, and a fluid cell constructed into the lower portion of the Reaction Chamber for testing the electrical conductivity of the leachate (presumably to contain electrolytes, such as MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl and other putative Martian salts). The electronics to drive the conductivity sensor was breadboarded and testing was initiated. A third unit was constructed to prove the fluids manipulation concept under nominal Mars atmospheric pressure (6 millibar). It was further determined that this unit should also be functional on a lab bench, *i.e.*, within one earth atmosphere (one bar) pressure. This additional requirement made development of working concepts difficult, because a high level of ambient pressure poses significant problems in fluid manipulation in small sealed systems. Figures 1 through 5 detail the Fluids Handling Breadboard and associated MACE test setup.



**Figure 1 MACE Fluids Test Unit #3 Schematic**

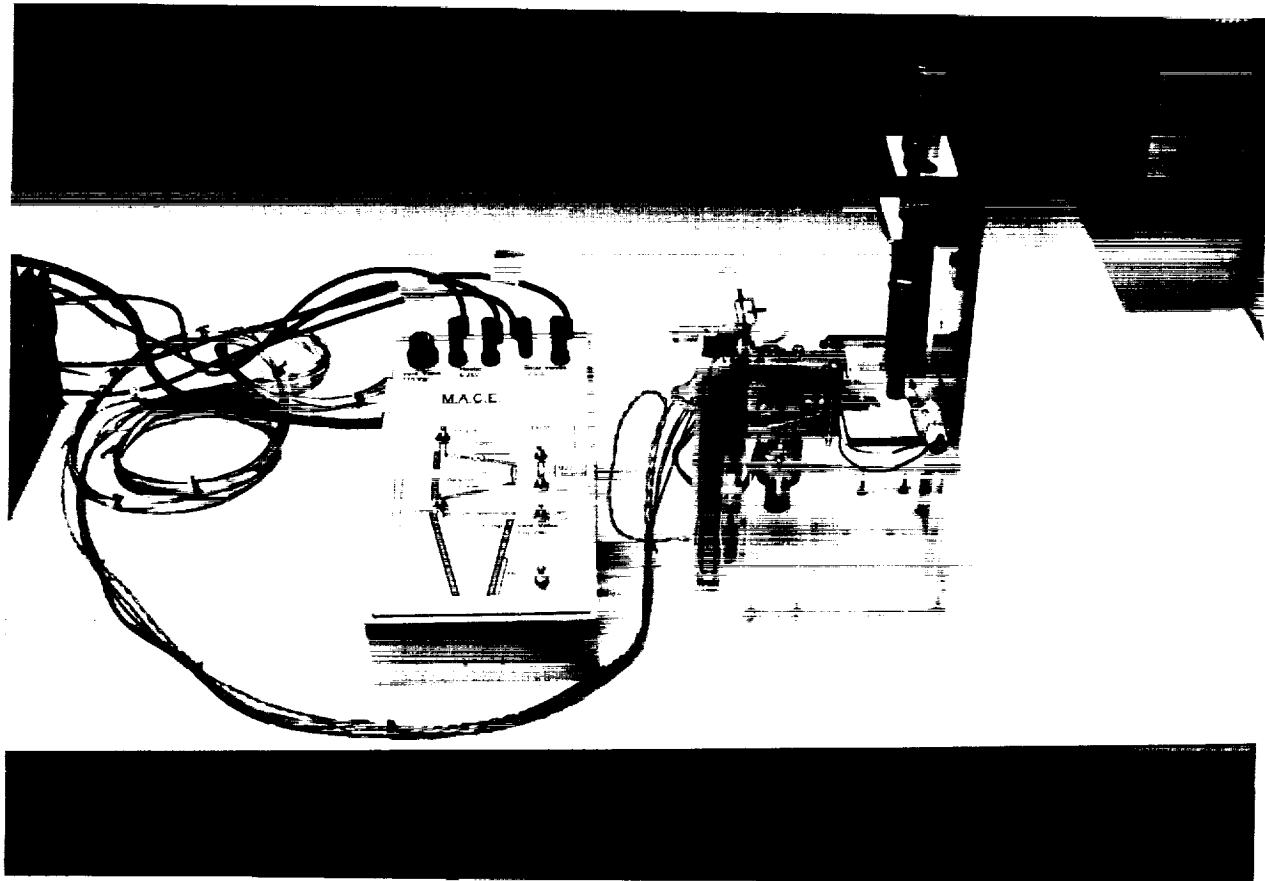
At Earth nominal pressure most small systems are either vented to atmosphere or use high pressure to overcome trapped air bubbles and allow fluid movement. In the MACE concept both the Reaction Chamber and the Sump are small fixed volume enclosures. Forcing fluid into and between these volumes increases the internal chamber pressure until the pressures of the delivery system and the internal volume are equal and fluid no longer flows. Using only the pressure head provided by gravity as a driving force in such systems is not practical. The pressure provided by one foot in height of water (pressure head) is equivalent to about one half pound per square inch (0.43 psi). Earth atmospheric pressure is ~13.1 psi in Denver. Since the chamber volume is small and fixed (~7 ml) the pressure increases as fluid begins to flow into the chamber. If the fluid movement is driven by an inch or so of pressure head, after a few drops of fluid have entered the chamber at earth normal pressure the internal pressure has been raised enough for flow to cease, (as occurred in the original concept). Since the inlet tube opening is very small (0.032" diameter), there is no way for the trapped air to escape, creating a "vapor lock" condition; fluid flow into the chamber is stopped.

To overcome this problem in a sealed system requires a higher delivery pressure from the Reservoir Volume to Metered Volume, and somewhat lower pressure to transfer fluid to the Reaction Chamber. This was accomplished by designing a weighted plunger system that displaced water in the reservoir as it was delivered to the Reaction Chamber. Both the Reservoir Volume and the Metered Volume in the third development unit use this principle.



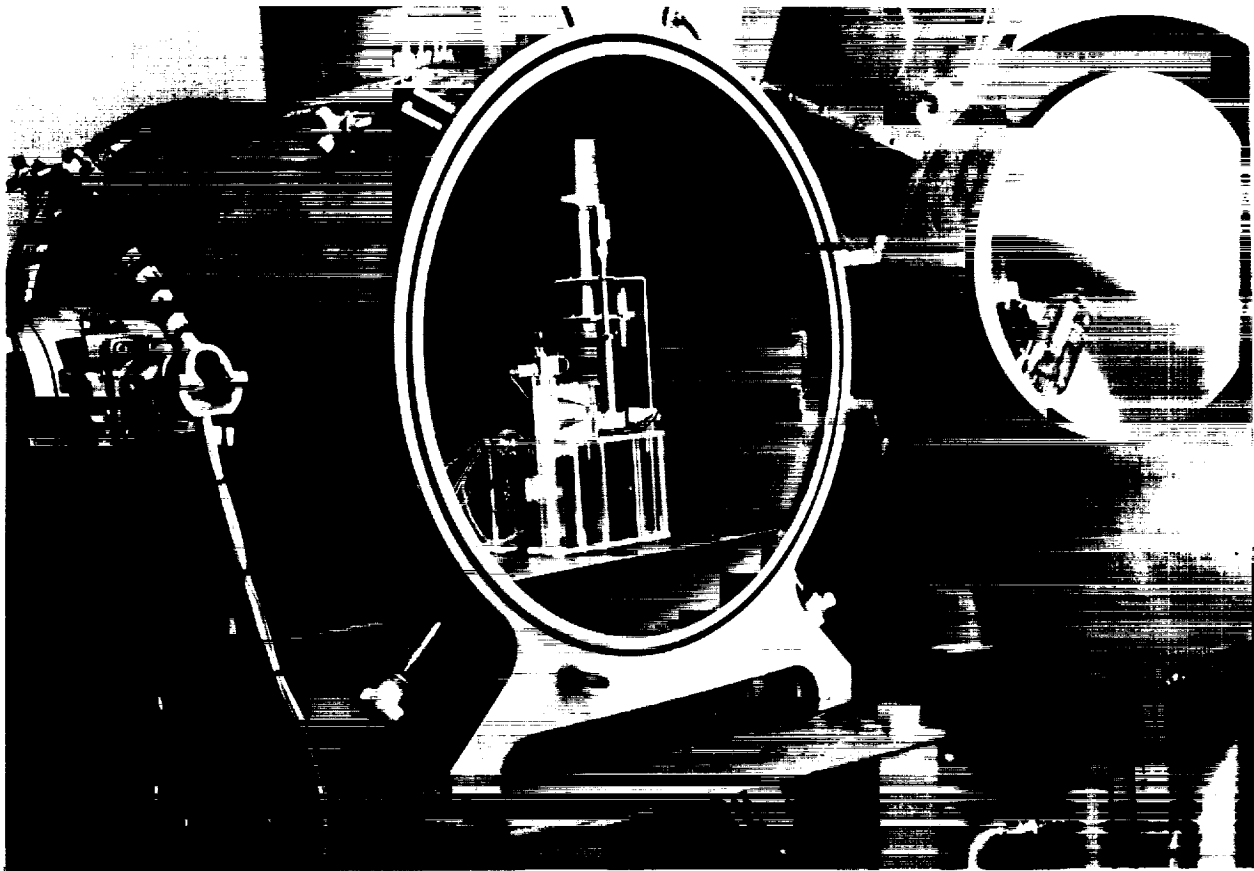
*Figure 2 MACE Fluids Handling Breadboard Unit #3*

The Reservoir Volume uses a plunger 0.705 inches in diameter, and a weight of 1.82 lbs. The Metered Volume has a plunger 0.250 inches in diameter, and a weight of 0.185 lbs. The pressure provided by these weights is 4.5 psi from the Reservoir Volume, and 3.3 psi from the Metered Volume. This is independent of whatever background atmospheric pressure exists around and within the unit. These are low pressures from a fluids handling sense, but are high enough to overcome the atmospheric problems encountered when operating on the lab bench. The fluid-handling valves are miniature solenoid valves (Lee #LFAA1201618H), similar to flight-like units, and can be enabled for remote operation, as required when testing under Mars conditions in a modified vacuum chamber. The breadboard construction in the third unit is modular to allow for future changes, modifications, and additions to the system without a complete rebuild, as was necessary with the first two units.



*Figure 3 Control Unit for Remote Operation of MACE Fluids Handling Breadboard*

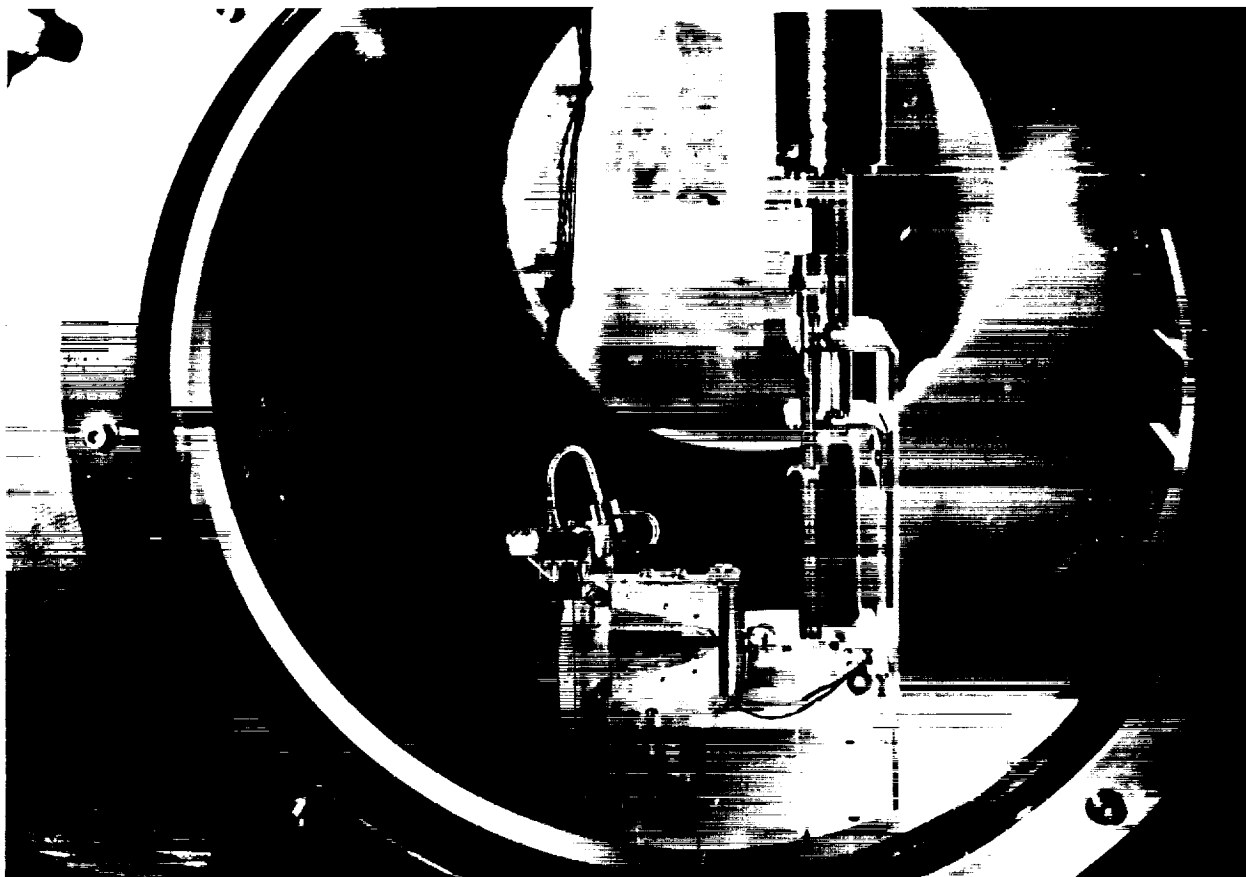
An alternative design was conceived to avoid the problems of friction between sealing surfaces of plunger and reservoir wall, which detracts from the total pressure applied to water in the system. The Reservoir Volume and the Metered Volume are both constructed using tubular elastomer membranes contained within separate cylinders, and each plunger acts to deform its respective membrane while providing pressure to the fluid. The membrane simply rolls from cylinder wall to plunger wall as the plunger descends. In operation this provides for a nearly frictionless method of hermetically sealing the reservoir as each plunger moves within its containing cylinder.



**Figure 4** *Mars Simulation Chamber Used for Low Atmospheric Pressure Testing*

This design simplifies the operation, allows accurate calculation of applied pressure, and does not require any factors for unknown fictional constants such as static, sliding, or compression set. A similar mechanism may be used on an actual flight instrument, but more suitable materials will be necessary than used in this proof of concept model, (*i.e.*, flight approved elastomer, Teflon coated phosphor bronze bellows, or other mechanisms and material currently under consideration).

The MACE unit #3 functions well in both atmospheric and simulated Martian pressures. Fluid is delivered first to the Metering Volume then to the Reaction Chamber. The time required to fill the Metered Volume from the Reservoir Volume is less than 5 seconds. The time to dispense this volume to the Reaction Chamber is between 1.5 and 2 seconds. There is an adjustment capability to change the volume dispensed through the Metering Volume, presently set at 2.08 ml. The time is approximately the same for bench top (1 atmosphere) or vacuum chamber (6 mbar) ambient pressure operation. On the lab bench, however, if the reaction chamber already contains the first injected aliquot of water, the internal pressure equalizes to the 3.3 psi of the Metered Volume before the second injection has finished flowing into the Reaction Chamber. There is no problem draining the Reaction Chamber at 6 mbar, because what little gas is left dissolves in the water and the partial pressure provided by the water itself (after being degassed by boiling) is adequate to allow the flow of water into the sump. There is enough background pressure in the reaction Chamber to drain the fluid into the sump once the sump is vented to ambient atmosphere.



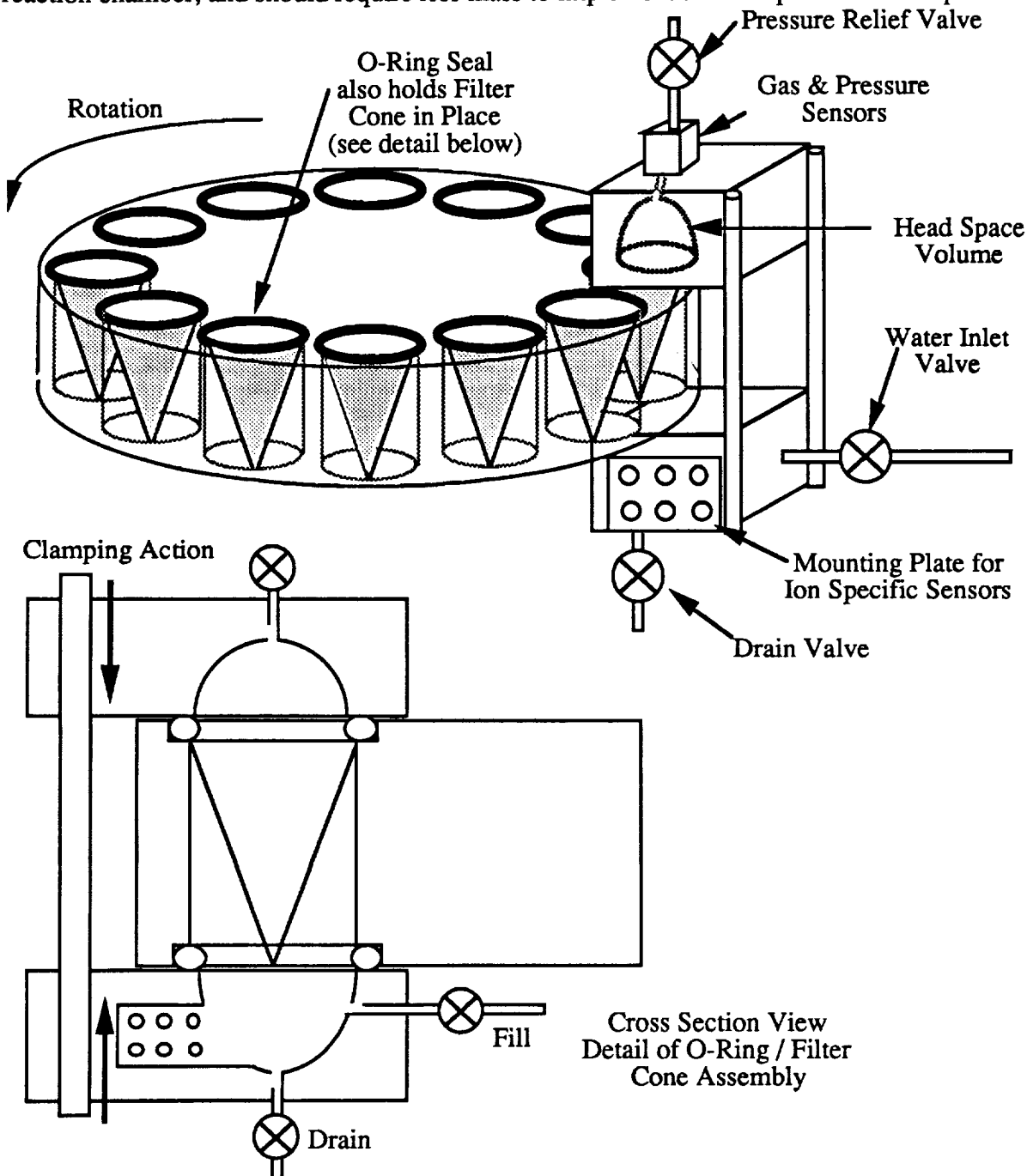
*Figure 5 MACE Fluids Breadboard Operational in Mars Simulation Chamber*

The sump vent valve is used to vent the sump to atmosphere in order to evaporate the water and allow XRF analysis of the water soluble regolith components. This valve is solenoid driven, but is a commercial pneumatic type solenoid valve, chosen for its availability and for the fact that it has a large ports and valve orifice. The large diameter tubing and orifice help speed up the evaporation of water for XRF analysis. On the lab bench the sump is simply removed and drained to discard or analyze the collected water.

The test unit #3 currently has a mercury manometer connected to the Reaction Chamber through a tee and valve. This allows pressure measurements to be acquired when gases are released or evolved from the soil samples under analysis. The valve also allows the Reaction Chamber and manometer to be vented as the system is evacuated during pump down in the vacuum chamber. The unit has been bench tested in one atmosphere, and also tested under Martian ambient pressures. The initial verification and operation of the fluid management system was very successful. Fluid flow was under excellent control; the sample chamber could be filled in small increments, and be held constant at any level. No back-pressures occurred under simulated Mars pressure; and chamber clean-up via evaporation/sublimation was very efficient and rapid. These tests also revealed additional areas that require attention, especially the generation of gas bubbles, which could act to prematurely wet the sample in the early humidification phase of sample analysis. Countermeasures to this are currently under consideration.



Alternative Fluids Handling Designs--As the design concept of the MESUR mission spacecraft matures, the interface between this instrument and the spacecraft also evolves. The current concept is for sample to be delivered to the science instruments for analysis, which simplifies the original MACE sample acquisition concept, where a drive tube was used to acquire regolith for analysis. The advent of a delivered sample allows a much less robust sample containment assembly to be used. Figure 6 shows one alternative concept, termed the MACE carousel concept, for analysis of 12 independent regolith samples using cones of filter paper to contain the regolith during aqueous humidification, dissolution, and analysis. This design has a smaller reaction chamber, and should require less mass to implement than the previous concept.



**Figure 6 MACE Carousel Concept**

## Aqueous Chemistry

Three areas of activity are reported in this section: (1) wet chemical analysis specifications, (2) test strip technology, and (3) Ion Selective Electrode (ISE) characteristics.

**Wet Chemical Analyses** -- Test kits were acquired for wet chemical (spectrophotometric) analysis of the ions Calcium, Chloride, Iron, Nitrate, and Sulfate. The analysis procedures were characterized in terms of sensitivity, error, complexity, analysis time, and colorimetric wavelength, as shown in Table 1. The chemistry associated with each of these analyses is based upon reacting the ion of interest with appropriate molecules to create a soluble complex that adsorbs light, *i.e.* creates a colored solution. The adsorption of light at a particular wavelength is then proportional to the concentration of the ion of interest by Beers law of optical absorption. Solutions of known ionic concentration are prepared and analyzed in parallel with the samples to calibrate the procedure, establish a linear range, and verify proper response.

**Table 1 Wet Chemical Ion Analysis Protocol Characterizations**

Ion	Sensitivity range (ppm)	Analysis error (%)	Number of reagents/steps	Analysis time (min)	Colorimetric wavelength (nm)
Ca <sup>++</sup>	5 - 300	4	3	10	540
Cl <sup>-</sup>	0.4 - 40	3	2	1	450
Fe <sup>++</sup>	0.04 - 4.0	0.1	1	3	565
NO <sub>3</sub> <sup>-</sup>	5 - 90	5	3	10	515
SO <sub>4</sub> <sup>- -</sup>	10 - 600	5	5	12*	515

\*incubate@ 40C

The concentration range for each of these analyses spans at most two orders of magnitude before becoming non-linear. If the linear range is exceeded appropriate dilutions of the sample must be performed and the analysis repeated. Each analysis is also dependent on temperature to varying degrees, and interference effects from other ions may be present. The wavelengths listed in Table 3 represents the adsorption maximum for the particular color complex formed, and thus the maximum sensitivity for each analysis. The adsorption peaks are fairly broad, spanning about 100 nm. As a result, a single wavelength intermediate to all analyses may be chosen for commonality with some loss of sensitivity.

**Ion Test Strips** -- Test strips were acquired to evaluate the technology applicability for autonomous determination of ions in aqueous solution. This type of test is inherently semi-quantitative, relatively sensitive, quick, and spans a concentration range from 1 - 250 ppm. The principle of operation is similar to wet chemical methods, and is based on a chemical reaction that either oxidizes or reduces a dye indicator that is chemically bound to the test strip. The result is a change in color that is proportional to the concentration of the ion of interest in the aqueous solution. The color produced by the reaction is compared to a scale of colors for rough determination of ionic concentration. The resolution obtainable using test strips is within an error margin of  $\pm 25\%$ , depending on the age and storage history of the test strips, presence of interfering ions, temperature of the solution, skill of the analyst in comparing colors, and prior knowledge of the test solution. These test strips are most applicable for a quick test to determine a rough order of magnitude for concentration of ions in solution.

Ion Selective Electrodes --When an ISE and a reference electrode are placed in an aqueous solution, a potentiometric cell is formed. The sensing half of the electrochemical cell (half cell) responds to ion activity (concentration) in a relationship described by the Nernst equation (1):

$$E = E_0 + 2.3 \frac{RT}{nF} (\log_{10} C) \quad (1)$$

where  
 E = developed electrochemical potential (V)  
 E<sub>0</sub> = standard potential of the system (V)  
 R = ideal gas constant (8.314 V•coulombs•mol/K)  
 T = absolute solution temperature (°K)  
 F = Faraday's constant (96493 coulombs)  
 n = number of electrons in the electrochemical reaction  
 C = concentration of ions in solution (M)

The 2.3RT/nF term can be reduced to a single slope factor at constant temperature for each electrode and reference electrochemical cell. The reference half cell also behaves according to the Nernst equation, but does not change potential with respect to the sensed ion. At constant temperature, each overall galvanic (ISE + reference) cell can be described using an equation in which the cell potential varies directly with the log of ion concentration in a straight-line manner, as shown in Equation (2).

$$E = V_0 + S * \log_{10}(C) \quad (2)$$

where  
 E = developed galvanic cell voltage (V)  
 V<sub>0</sub> = voltage offset (V)  
 S = slope (V/decade of ion concentration)  
 C = concentration of ions in solution (M)

Comparison of Ion Quantitation Methods -- The three methods for measurement of ions in solution considered for use in MACE have been evaluated, and are summarized in Table 2.

**Table 2 Ion Measurement Methods Applicability Study**

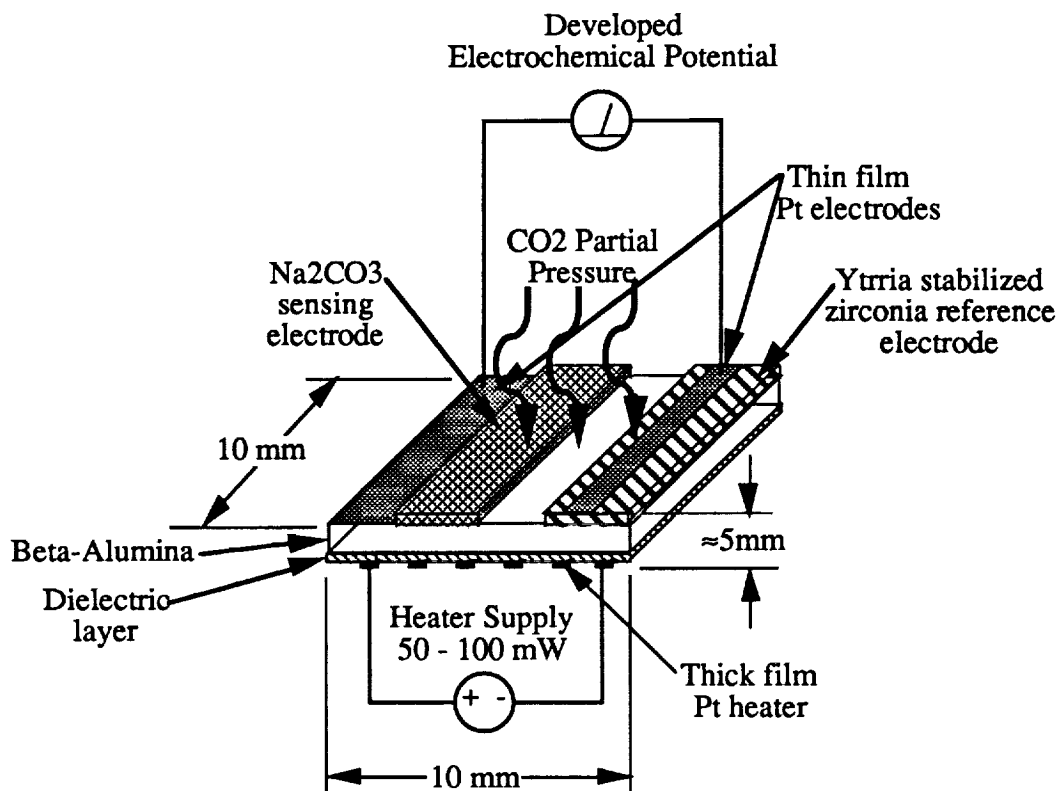
Method	Dynamic Range	Resolution	Type of Analysis Output	Relative Complexity
Ion Selective Electrodes	10 <sup>5</sup>	±5%	voltage	simple
Test Strips	10 <sup>2</sup>	±25%	color comparison	intermediate
Wet Chemistry	10 <sup>2</sup>	±5%	colorimetric	complex

The method of choice for ion analysis is Ion Selective Electrodes, due to the large dynamic range, resolution, electrical signal output, and simplicity. The other two methods both require a spectrophotometer to measure developed color and convert the ion concentration to an electrical signal. This involves a substantial increase in instrument complexity relative to that required for Ion Selective Electrodes.

### Gas Sensing Electrodes

We have established relationships with two companies experienced in custom fabrication of aqueous ion microsensors, Teknekron Inc. (Menlo Park, CA), and Stanford Research Institute (SRI) International (Stanford, CA). Over the last year we have begun preliminary discussions concerning the goals of the MACE project, and possible sensor implementations. In a related

Martin Marietta project, a micro-scale  $\text{CO}_2$  solid state electrochemical gas sensor in a planar configuration is being developed. This sensor is directly applicable to the MACE project, and will be capable of sensing the partial pressure of  $\text{CO}_2$  over a range of from .01 to 100 mbar, using less than 80 mW of power. Figure 7 shows a schematic representation of a candidate sensor design. The response time is expected to be on the order of 0.5 seconds, with an expected operational and shelf lifetime of at least 4 years.



**Figure 7** Martin Marietta/SRI International Micro-scale  $\text{CO}_2$  Gas Sensor

The electrode functions by producing a voltage that is proportional to the partial pressure of  $\text{CO}_2$  according to the Nernst equation (1).  $\text{CO}_2$  gas dissolves into the  $\text{NaCO}_3$  layer, and changes the half cell potential at the  $\text{NaCO}_3$  | beta alumina interface. The zirconia reference half cell potential remains constant, and the overall galvanic cell potential changes in proportion to the logarithm of the  $\text{CO}_2$  partial pressure.

Larry Mason, a MACE Co-I, visited SRI International in mid April '93, for discussions concerning this sensor. During this visit, additional topics concerning custom fabrication of micro-scale ISE's for measurement of pH,  $\text{Ca}^{++}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^{++}$  ions in aqueous solution were also discussed. These ions represent important constituents in the Martian regolith. These sensors are not all available commercially, and none are available in the micro-scale. Other topics of discussion at SRI included sensor repeatability, lifetime, electrolyte materials suitability for MESUR/MACE, and selectivity and interference issues.

SRI International developed the oxygen sensor that is currently used in the pollution control systems on automobiles manufactured in the US. This sensor is also applicable to MACE, particularly for measurement of the liberated oxygen superoxide decomposition. The relative amount of effort involved in customizing this relatively mature sensor for use in MACE was also discussed. The normal operation of the present sensor is within the exhaust gases from a

combustion engine. It is possible to apply this technology to the MACE application with the addition of a separate heating circuit and appropriate hardware fixtures to allow mounting. It was estimated that this effort will involve one to two man-months of labor to complete.

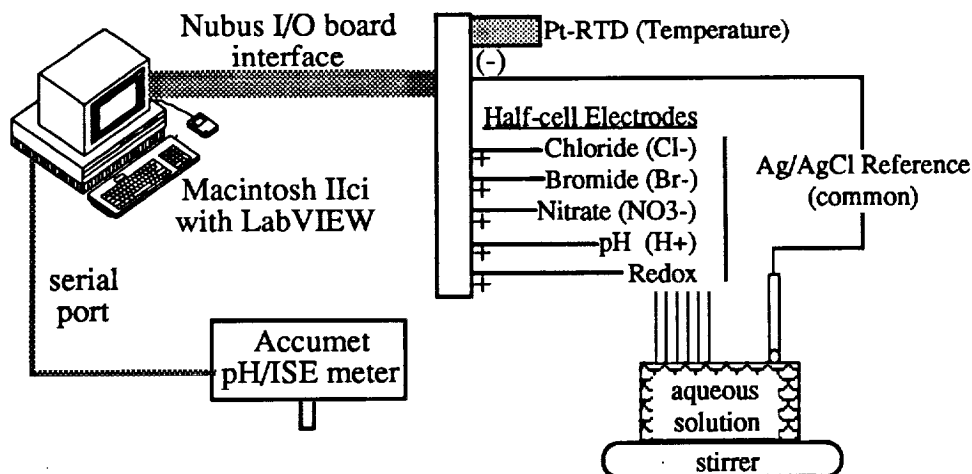
### Development of the Ion Selective Electrodes Test Facility for MACE

A facility for characterization of and experimentation with Ion Selective Electrodes (ISE) was developed during the first year activity using Martin Marietta Capital Equipment funding. This facility was designed to characterize the performance of ion selective electrodes and to measure the kinetics of ionic dissolution from various geochemical regolith samples and analogs. A vendor search was initially conducted to identify commercially available mini-scale electrodes for sensing the ions of interest in aqueous solution. The associated interface electronics was also procured to enable development of a multifunctional array of sensors. Table 3 lists the electrodes included in the facility, along with the specific ion sensitivity, sensor size, and supplying vendor.

**Table 3 Ion Selective Electrodes in the MACE ISE Facility**

<b>Ion Selective Electrode (ISE) half cell</b>	<b>Sensor Size (mm)</b>	<b>Specified Sensitivity Range (mM)</b>	<b>Vendor</b>
Chloride (Cl <sup>-</sup> )	1 dia x 4 len	0.0003 - 70	Lazar Scientific
Bromide (Br <sup>-</sup> )	1 dia x 4 len	0.0004 - 80	Lazar Scientific
Nitrate (NO <sub>3</sub> <sup>-</sup> )	12 dia x 110 len	.01 - 1000	Orion Scientific
pH (H <sup>+</sup> ) (polymer body)	2 dia x 4 len	2 - 12	Lazar Scientific
pH (H <sup>+</sup> ) (glass body)	1.2 dia x 2 len	2 - 12	Microelectrodes Inc.
Oxidation Reduction (Eh)	2 dia x 3 len	-300 to +300 mV	Lazar Scientific
<b>Reference Electrode half cells</b>	<b>Electrode Size (mm)</b>	<b>Electrochemical half cell</b>	<b>Vendor</b>
Silver Chloride	12 dia x 200 len	Ag/AgCl	Fisher Scientific
Calomel	12 dia x 200 len	Hg/Hg(l)Cl	Fisher Scientific
Double Junction	3 dia x 180 len	Ag/AgCl	Microelectrodes Inc.

ISE Interface Development -- Figure 8 shows a schematic diagram of the facility as interfaced through a Macintosh Mac IIci computer with LabVIEW instrument control software for data acquisition functions.



**Figure 8 MACE ISE Facility Interface Schematic**

A separate single channel high impedance electrochemical meter (Fisher Accumet 900) is also shown interfaced to the computer. This meter is not part of the facility, but is used for external verification of single electrode potentials measured through the computer interface electronics. A Resistance Temperature Detector (Platinum RTD) is also interfaced through appropriate electronics to accurately measure the solution temperatures, and to monitor the heats of dissolution associated with various salts.

Software was developed to enable acquisition of electrochemical data from the various electrodes. The LabVIEW instrument control package was used to develop software algorithms to acquire the electrochemical signal from the electrodes and display the data on a screen based strip chart recorder. The method used for calibration of the electrodes was to immerse the electrodes in a series of calibration solutions while monitoring the electrical signals. When the transients had died out, the steady state electrochemical potential was used to construct calibration and interference curves. Figure 9 shows the front panel of the data acquisition program is shown, where a screen-based strip chart records the voltage (y-axis) of each ISE at user selectable time intervals (x-axis). The program allows data to be acquired and stored to files for further analysis on either a continuous basis for dissolution experiments, or on an intermittent basis for calibration and interference studies.

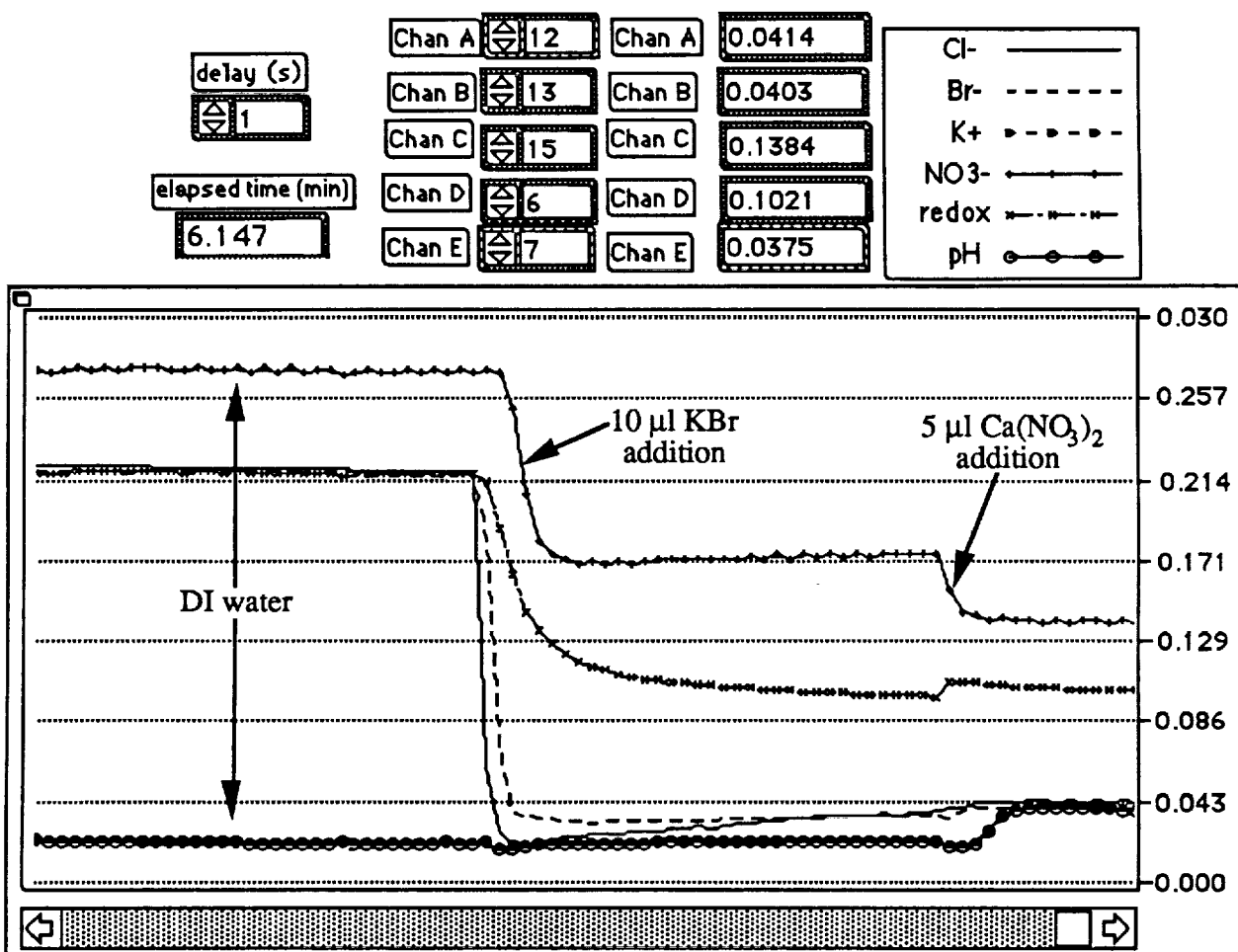


Figure 9 LabVIEW Front Panel Strip Chart Displaying ISE Transient Data

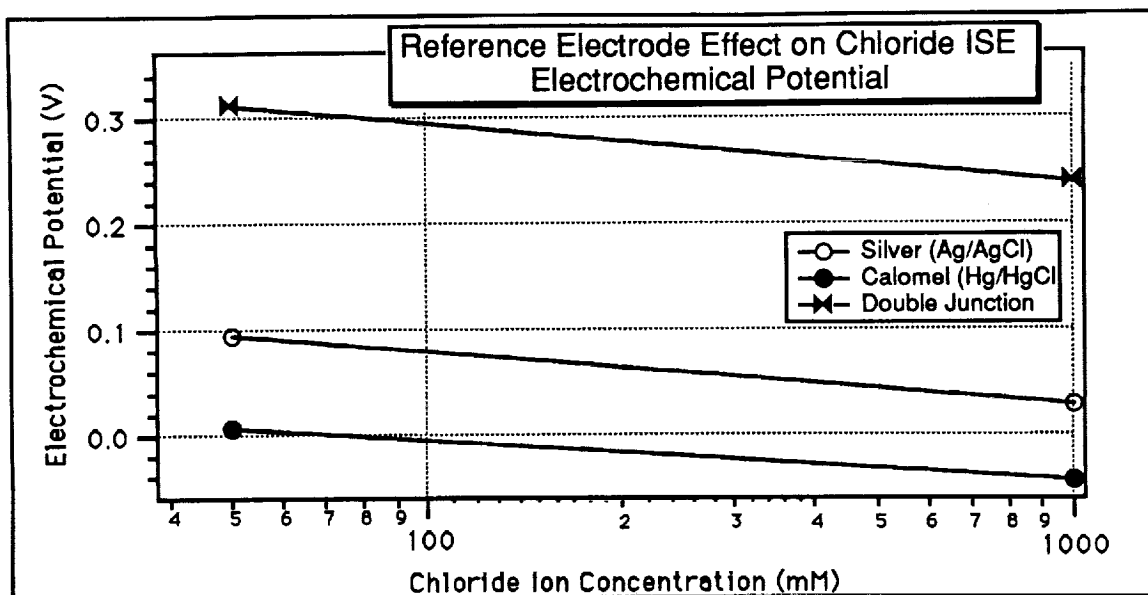
The data shown on the strip chart represents the voltage transients resulting from addition of 10  $\mu\text{l}$  of 1M KBr (first transient) and 5  $\mu\text{l}$  of 1M  $\text{Ca}(\text{NO}_3)_2$  (second transient) to 10 ml of deionized water. The response indicates the signal generated for the concentration transient from 0 to 1 mM  $\text{Br}^-$  and 0 to 1 mM  $\text{NO}_3^-$ . The data shown were acquired at one second intervals, showing the typical response where all transients from step changes in concentration settled out within 10 seconds.

The extremely high electrical impedance inherent with these electrochemical cells ( $\approx 10^{10} \Omega$ ) necessitates the use of input electronics having several orders of magnitude greater input impedance ( $>10^{12} \Omega$ ) to accurately measure the developed electrochemical potential. This type of high impedance circuitry is typically employed in analog laboratory meters, such as the Fisher Accumet 900 meter used in the MACE ISE facility to verify the computer acquired data. This type of meter is limited to monitoring a single ISE at a time, however, and each ISE requires a dedicated reference electrode.

The instrumentation amplifier on the nubus I/O board in the Macintosh has an input impedance on the order of  $10^9 \Omega$ , too low to be used in an analog mode. A special mode for time-sequenced data acquisition was developed under Martin Marietta internal research to overcome this limitation and allow multiple electrodes to be measured using the single instrumentation amplifier and associated multiplexer circuitry resident on the I/O board. In this mode all non-selected channels are gated to an extremely high input impedance, increasing the impedance seen by the electrodes during non-data acquisition periods. The time averaged, or overall effective input impedance seen by any one electrode is much higher than the nominal instrumentation amplifier input. Data acquired in this manner was very consistent for all electrodes tested, and correlated well with single electrode measurements using the Fisher laboratory ISE meter. The circuitry and driver algorithm developed has the added advantage of requiring only a single reference electrode for all the ISE's interfaced, as opposed to the standard laboratory case where one reference electrode is required for each ISE. The I/O board is configured in the single-ended mode, and has capability for up to 16 separate ISE's to be multiplexed for data acquisition using a single reference electrode.

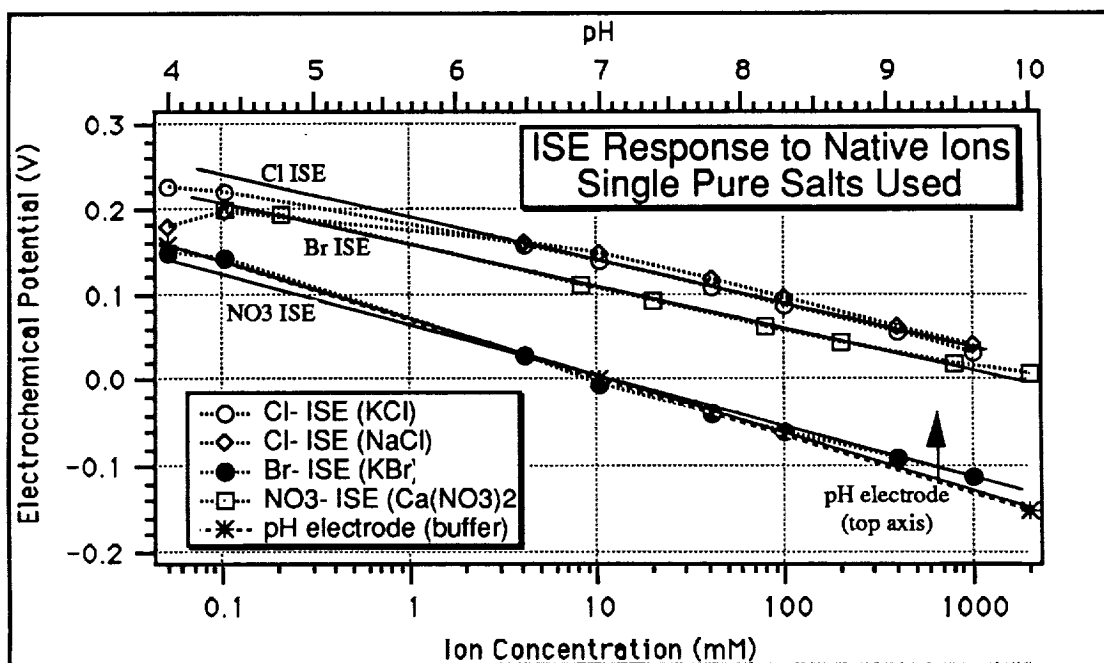
The offset voltage for each galvanic cell is a function of the type of reference electrode used. Preliminary experiments were performed to characterize the various ISE and reference electrodes, establish calibration coefficients, and to determine selectivity and interference parameters. Initially three reference electrodes (silver -  $\text{Ag}|\text{AgCl}$ , calomel -  $\text{Hg}|\text{HgCl}$ , and an  $\text{Ag}|\text{AgCl}$  double junction gel electrode) were interfaced for data acquisition and tested using the chloride ISE to determine the relative offset voltages. Data was recorded for the potential produced when immersed in two different concentrations of a chloride salt (KCl), as the steady state voltage after the transients had died out. No stirring was used in this preliminary experiment, although the readings changed significantly when stirring was used. Figure 10 shows a semi-logarithmic plot of the data resulting for each of the three reference electrodes.

The voltage offset ( $V_o$ ) is shown to be a characteristic of the reference electrode used. The slope of the lines is a function of the ISE half cell, and is consistent among the three traces at about 50 mV/decade of ion concentration. Further experiments were performed using only the Silver ( $\text{Ag}|\text{AgCl}$ ) reference electrode because the overall potential developed for all ISE's tested was closest to zero, allowing the highest measurement gain to be used when acquiring the data.



**Figure 10** Effect of Reference Electrode on Cl<sup>-</sup> ISE Performance

ISE Characterizations -- The electrochemical response from the five commercially available ISE's has been characterized in the MACE ISE test facility, using the data acquisition software and protocols described in the previous section. The voltage developed by each galvanic cell was measured during simultaneous exposure to single salt solutions of varying ionic composition and concentrations ranging from 0.05 millimolar (mM) to 1.0 molar (M). The data obtained from this procedure is shown in Figure 11. The plot shows the single ISE concentration dependent voltage response to individual ions in solution, using the salts: KCl, NaCl, KBr, Ca(NO<sub>3</sub>)<sub>2</sub>, and commercial pH buffer solutions.



**Figure 11** Single Salt Solution ISE Responses

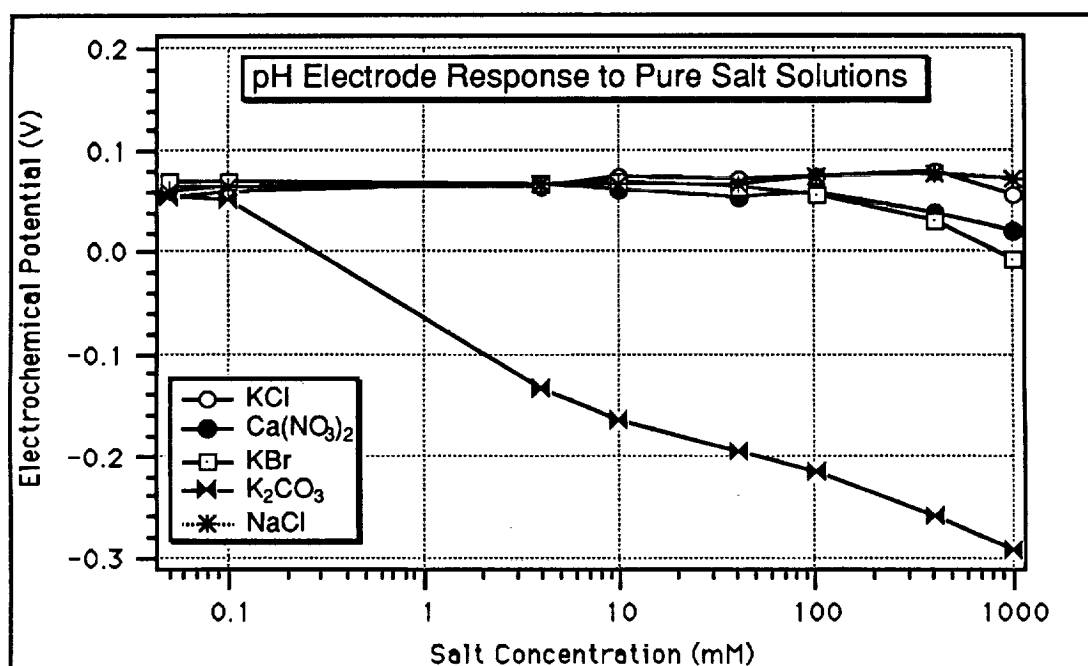


Calibration equations were developed for each ISE to its native ion (e.g. chloride ISE response to  $\text{Cl}^-$  ions) by performing a least squares regression fit to an equation of the form shown for equation (2). Only data in the linear portion of the resulting calibration curves were used, with the minimum concentration noted where the linear relation holds. Table 4 summarizes the coefficients obtained in this analysis, and lists the minimum concentration for which the derived linear relation holds.

**Table 4 Regression Fit Coefficients for ISE's and Native Ions**

ISE/ion	$V_o$ offset (V)	Slope (V/decade)	Minimum linear Concentration (M)
chloride	0.04166	-0.05151	0.0005
bromide	-0.1200	-0.06281	0.0001
nitrate	0.01402	-0.04738	0.0001
hydrogen	0.3611	0.05125	$1.0 \times 10^{-10}$

Most of the salts tested had no effect on the pH electrode, as shown in Figure 12. This is to be expected, because there is very little buffering capacity or hydrogen ion effect associated with pure salt solutions. The exception to this is  $\text{K}_2\text{CO}_3$ , which dissociates into potassium and carbonate ions in aqueous solution, and reacts with water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), an acid that has a definite effect on pH. The pH electrode was calibrated using commercially available pH buffer solution.



**Figure 12 Single Salt Solution Effect on pH Electrode**

**ISE Interference Effects** -- The transient voltage responses shown previously in the strip chart traces of Figure 3 indicate the degree of interferences that will be present in a solution containing more than one ion. The addition of  $\text{Cl}^-$  ions caused all ISE's except the pH electrode to change in electrochemical potential, not just the  $\text{Cl}^-$  ISE. This is indicative of a problem in ISE selectivity among ionic species, and is inherent to any ISE design. The name implies this type of response: ion *selective* electrode (not ion *specific* electrode). The extent of this problem is apparent in Figure 13, where the Br ISE response to various salt solutions is shown. A Nernst like response is apparent for all ions tested, but the onset of electrochemical response is very ion specific and

concentration dependent. Each of the ISE's tested showed responses similar to this, but each had an apparent selectivity for its native ion (e.g. the Br ISE had a preferential response for Br<sup>-</sup> ions). It should be possible to construct an iterative algorithm to deconvolve the overall ion concentrations based on the input from each ISE. The approach to this problem is discussed in the next section: Plans for the Coming Year.

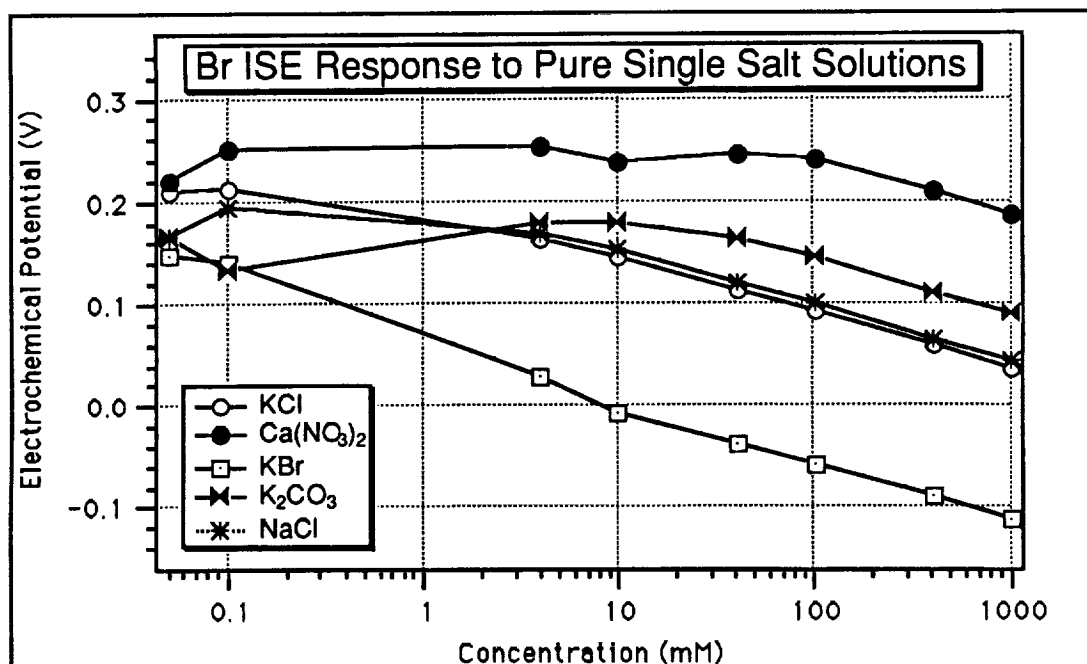


Figure 13 Br- ISE Response to Various Salt Solutions

### Salt Dissolution Kinetics Experiments

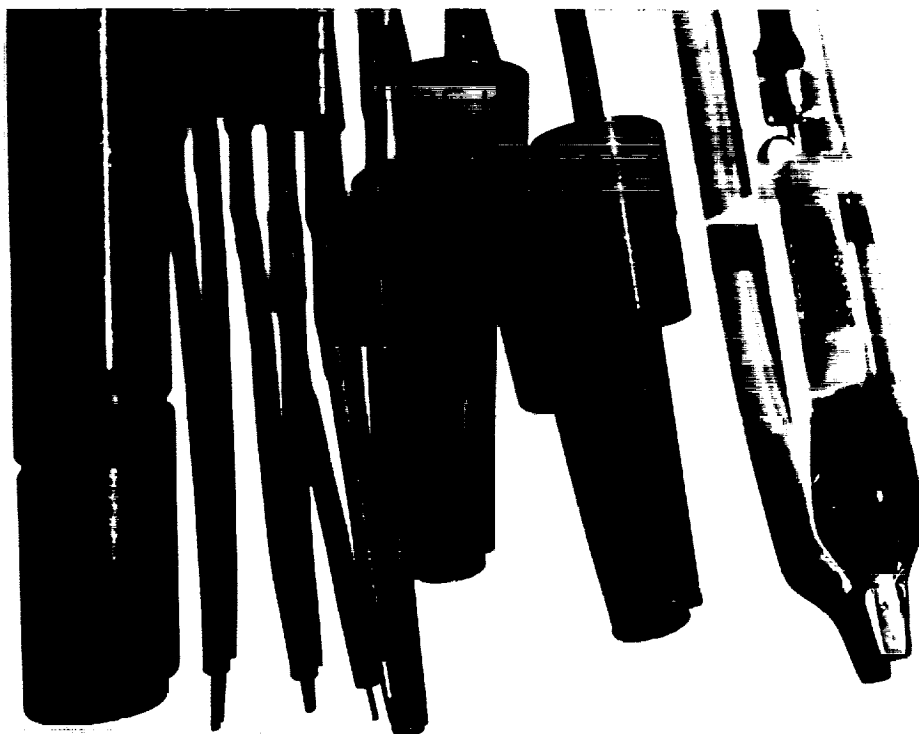
Pathfinding experiments were performed to demonstrate measurement of the kinetics of salt dissolution. The sensors used in these experiments included an RTD temperature sensor and seven Ion Selective Electrodes (ISE). Figure 14 shows a photograph of the commercially obtained ISE's and reference electrode used in these aqueous ion dissolution experiments.

**Experimental Procedure**--Four pure salts were used in the experiments to provide a substrate for measurement of dissolution kinetics: {KBr, NaCl, FeCl<sub>2</sub>, & Ca(NO<sub>3</sub>)<sub>2</sub>}. In preparation for the experiments, the electrodes were placed in de-ionized water and allowed to equilibrate. The salts were weighed and enveloped within a single filter paper in preparation for aqueous extraction. The experiment began when the filter paper was immersed in the water, although data was acquired prior to this to establish baseline electrode potentials. The extraction was performed in 15 ml total aqueous solution volume, and stirring was included using a miniature magnetic stir bar measuring 1 mm diam by 5 mm long. The stirring action allowed convective mixing to aid the dissolution process, and minimized the concentration gradients present in the aqueous solution as the salts dissolved. Figure 15 shows the results of one dissolution experiment, where both the developed electrochemical potential (left axis) and solution temperature (right axis) are plotted as a function of time. The initial dissolution transients are detailed in the top data plot, and the entire experimental data shown in the lower plot.

It is apparent that the dissolution of this salt mixture is endothermic, because the temperature decreased by more than two degrees centigrade. Once the dissolution reaction was complete, the temperature began to rise due to heat input from the ambient environment and the stirring apparatus.

The total mass of salt dissolved in the experiment was 4.1 g, split among the four salts to achieve final ion concentrations in 15 ml of solution as follows: 1M  $\text{NO}_3^-$ , 1.3M  $\text{Cl}^-$ , 0.3M  $\text{Br}^-$ , 0.3M  $\text{K}^+$ , 0.5M  $\text{Fe}^{++}$ , and 0.5M  $\text{Ca}^{++}$ .

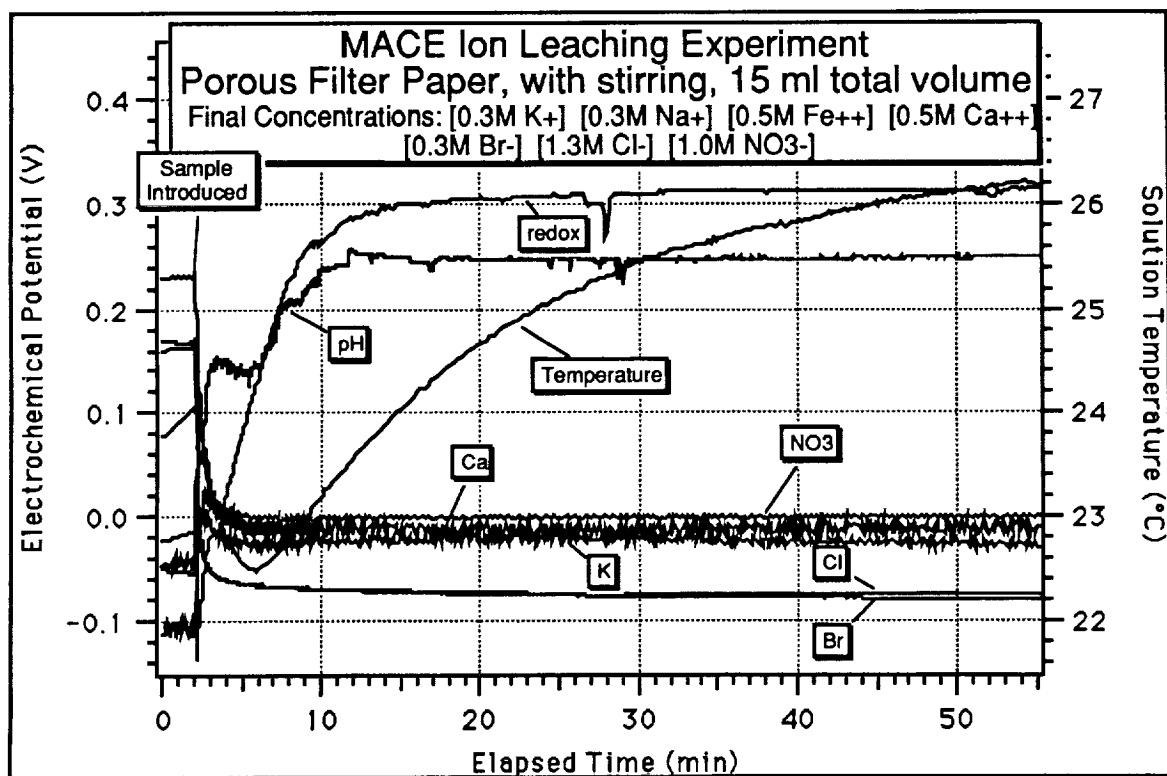
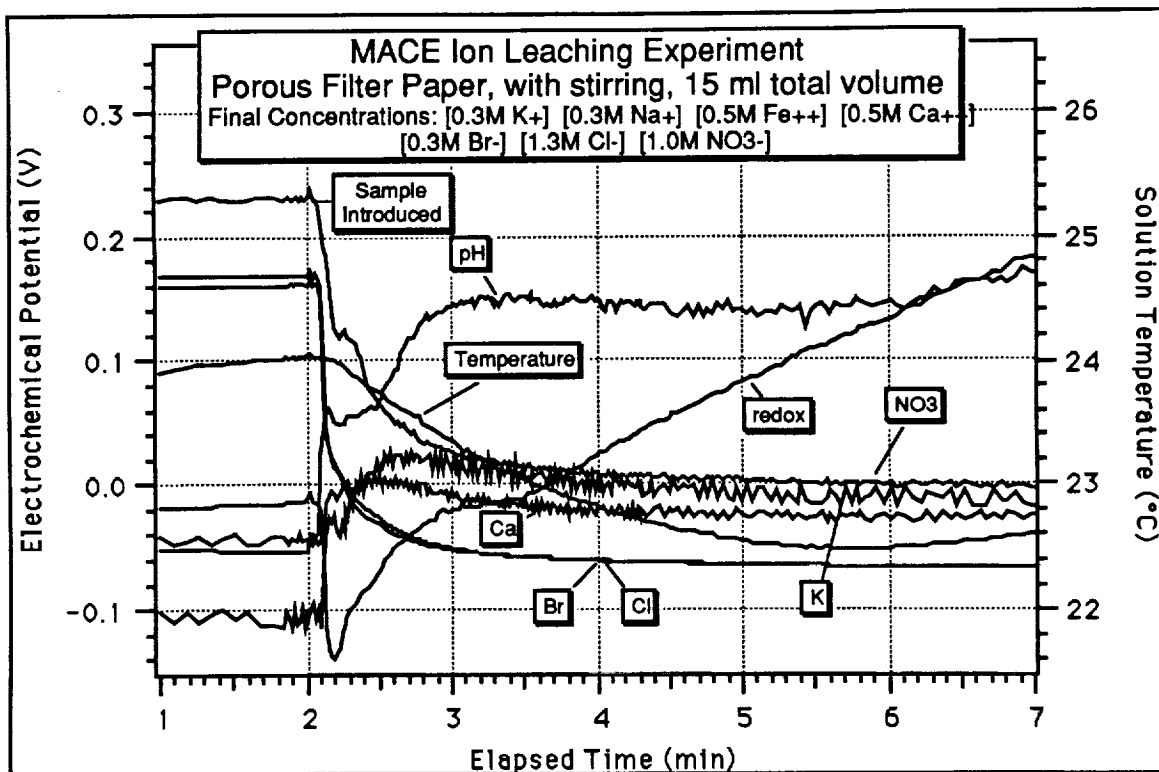
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**Figure 14 Ion Selective Electrodes Used in Aqueous Dissolution Experiments**

*The electrodes shown (left to right) are:  $\text{NO}_3^-$ , oxidation reduction,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Ag/AgCl}$  reference electrodes*

There are interferences between and cross sensitivities present among the various ISE's. Single and binary solution measurements have shown that these effects are significant, and if not accounted for, may lead to erroneous concentration determinations. The primary interfering action is due to differences in ion activities among the dissolved species, defined as the *effective* ion concentration. This may differ from the *actual* ion concentration by an amount depending on the exact composition of the total solution. In the case of an unknown sample, it is desirable to use an *ionic strength adjustment (ISA)* solution to set the activity of the solution, minimize the interferences between ISE's, and maximize the selectivity of each ISE to its native ion. The optimal composition of the ISA solution has not yet been determined, but will minimize interferences among the specific suite of ISE sensors chosen for use in MACE. No ISA solution was used in these experiments, and the concentration estimates derived from calibration of the ISE's using single salt solutions are not applicable. The steady state electrochemical potentials shown in Figure 15 do correspond to the actual concentration values, however, once the interference and selectivity effects are taken into account. The pH and oxidation/reduction (redox) ISE show the highest selectivity, and function mostly independent of total solution ionic strength. The steady state (final value) electrochemical potential value for pH corresponds to 2.2, and the final oxidation reduction potential is +0.31 V.



**Figure 15 Aqueous Dissolution Experiment Kinetics Data**  
 top) Initial Dissolution Transient Detail bottom) Entire Experiment Dissolution Data

These experiments were performed using a commercial macro-scale reference ( $\text{Ag}|\text{AgCl}$ ) electrode. The utility of reference cells in a micro-configuration is also currently being investigated. A comparison of the electrode types is shown in Figure 16, with the large liquid electrolyte cell used in these dissolution experiments shown on the left.



**Figure 16** *Ag|AgCl Reference Electrodes Under Evaluation for MACE*

The smaller electrodes shown in Figure 16 are also  $\text{Ag}|\text{AgCl}$  cells, but are all solid state and require no liquid electrolyte. These micro-scale reference cells are manufactured for the medical industry as disposable electrodes for *in-vivo* use, and are commercially available at low cost. An initial evaluation in combination with the ISE's used above has shown stable response in very dilute salt solutions, similar to that of the macro-scale reference cell used in the experiments. There is a voltage offset relative to the liquid electrolyte cell, but the offset is constant ( $\approx -213 \pm 5$  mV) for all ISE's tested. A constant voltage offset is expected between reference electrodes, as the function is to provide a reference electrochemical half-cell to compliment the sensing ISE and complete the electrical circuit. Separate and independent calibration curves are required for each ISE and reference electrode combination to insure maximum ISE sensitivity, selectivity, and accuracy.

#### **PLANS FOR THE COMING YEAR**

The development effort will continue in parallel efforts for the next year, continuing the two major areas begun this year, and adding the additional areas of regolith sample handling, containment, and overall instrument design. The two initial areas of physical fluids handling and aqueous chemistry sensor development and characterization will remain independent until the third year, when an integrated, computer controlled breadboard will be developed. Specific plans for each of the development efforts are detailed in the following sections.

### **Fluids Handling**

A number of additional tests will be performed to complete the fluid management system. These include an implementation of a spring-loaded bellows or other suitable drive for the reservoir and metering volumes. Our approaches will be to achieve a high reliability, no "moving parts" (as in sliding or ratcheting mechanisms). We have now shown that this is feasible using the valves to control flow and pressure heads maintained by dissolved gases or pre-planned head space pressurant gas.

### **Regolith Sample Handling**

The specific requirements for the MACE regolith sample tube depend on the way that the sample is acquired. If the regolith enters MACE through an entry port, delivered via a MESUR Sample Delivery System, the tube need be much less robust than if it is used in a "coring" mode. In contrast to the situation when this proposal was first submitted, this is indeed now the case. Recent JPL documents state that the method of acquiring samples for soil analysis experiments will be a MESUR lander facility capability, presumably a sampling arm. A disk sample cup with porous base is now possible. The requirements definition for the porous membrane will include a survey of materials and characteristics in terms of mechanical strength, porosity, surface tension effects, catalytic and chemical reactivity in aqueous solution, commercial availability, and geometrical considerations. Candidate materials will be procured and tested in the MACE ISE facility to characterize the material specific dissolution kinetics as described in the next section.

The design of the sample tube manipulation subsystem is also dependent on the specific mode of sample acquisition, although to a lesser extent than the tube itself. Preliminary designs and concepts for this subsystem were initiated in the first year, and will be further developed for use in the third year MACE breadboard.

### **Aqueous Chemistry**

There are several issues that must be addressed to establish the validity of ISE's for use in a space flight instrument (*i.e.* MESUR/MACE). One such issue involves the development and integration of micro-scale reference electrode(s) that are capable of withstanding the rigors of launch and the environmental extremes likely to be encountered during an interplanetary mission. The factors associated with different electrode types will be determined, and the feasibility of using more than one reference electrode will be investigated. This could allow redundant measurements to be acquired for each ISE, as well as providing an internal electrical calibration signal by measuring the potential between the two reference half cells (voltage is independent of ionic composition). The solid electrolyte reference cells described earlier will be fully characterized and evaluated for use in MACE.

Acquisition of New ISE's -- The commercial ISE's for  $\text{Ca}^{++}$  and  $\text{K}^{+}$  that have recently been procured will be further characterized. Calibration factors will be derived for these new electrodes, and they will be used in the cross sensitivity and interference studies.

ISE Interference and Cross Sensitivity Studies -- A systematic approach will be used to determine the cross sensitivity and interference effects between all ISE's and candidate ions. This will involve exposing the array of ISE's to many combinations and concentrations of binary ionic solutions and recording the ISE electrochemical potentials. Once the relative crosstalk factors are known, it should be possible to develop algorithms that can iteratively calculate the ionic composition of an unknown solution based on the electrochemical inputs from all of the ISE's. Ionic concentrations may then be determined in an iterative solution to the simultaneous equations that describe the behavior of each electrode in relation to all others.

The data returned from the instrument need be only the voltage for each electrode (perhaps for each of two reference electrodes), the iterative concentration calculations can be performed on Earth. The utility of Ionic Strength Adjustment (ISA) solutions will also be investigated and experimentally tested.

**Kinetics of Dissolution Experiments** -- Experiments will continue, and further kinetic data will be acquired for the dissolution of pure salts, combinations of salts, and regolith analogs using the MACE ISE test facility. The kinetics will first be characterized for the optimal case where a highly porous membranes or filter paper is used for containment of the solids and salts. The effects associated with other materials of increasing resistance to dissolution (*i.e.*, thicker walls, more robust materials) will be measured, and used as input for the regolith sample containment requirements definition.

**Overall Instrument Design** -- The areas of study listed above overlap considerably, for example concepts must be developed to maintain a "wet" electrical interface on the electrodes during the interplanetary voyage and between analyses, and to provide capability for calibration activities prior to each analysis. These issues involve both the fluids handling and electrode characteristics areas of study. The issues that overlap will be addressed in activities associated with the overall instrument design, where the driving requirements will be defined and prioritized. A working design concept for the integrated MACE breadboard will be produced that includes the comprehensive knowledge gained through the studies listed above. This design will be used as the baseline for the breadboard instrument to be developed in the third year of this contract.

## **CONCLUSION**

Excellent progress has been made at minimal cost in developing the MACE concept. Many of the design concept details have now been confirmed. Much work remains in firming up the sensor types most promising at this time and identifying future development work that could have important ramifications for this experiment. No other instrument that has so far been proposed for MESUR or other Mars surface mission has the sensitivity to numerous high-priority components thought to be present in Martian soils. In addition, many of the chemical and physical measurements that are proposed cannot be accomplished in any other way than by wetting selected samples of Martian soil.

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<p>16. Abstract MACE is designed to conduct a variety of measurements on regolith samples, encompassing mineral phase analyses, chemical interactions with H<sub>2</sub>O, and physical properties determinations. From these data, much can be learned or inferred regarding the past weathering environment, the contemporaneous soil micro-environments, and the general chemical and physical state of the Martian regolith. By analyzing both soil and duricrust samples, the nature of the latter may become more apparent. Sites may be characterized for comparative purposes and criteria could be set for selection of high priority materials on future sample return missions.</p> <p>Progress for the first year MACE PIDDP is reported in two major areas of effort:            (1) fluids handling concepts, definition, and breadboard fabrication            (2) aqueous chemistry ion sensing technology and test facility integration</p> <p><b>Fluids Handling Breadboard</b>            A fluids handling breadboard was designed, fabricated, and tested at Mars ambient pressure. The breadboard allows fluid manipulation scenarios to be tested under the reduced pressure conditions expected in the Martian atmosphere in order to validate valve operations, orchestrate analysis sequences, investigate sealing integrity, and to demonstrate efficacy of the fluid handling concept. Additional fluid manipulation concepts have also been developed based on updated MESUR spacecraft definition.</p> <p><b>Ion Selective Electrode Test Facility</b>            The Mars Aqueous Chemistry Experiment ISE facility was designed as a testbed to develop a multifunction interface for measurements of chemical ion concentrations in aqueous solution. The interface allows acquisition of real time data concerning the kinetics and heats of salt dissolution, and transient response to calibration and solubility events. An array of Ion Selective Electrodes (ISE) has been interfaced and preliminary calibration studies performed.</p>			
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